

GASIFICATION OF MONTANA LIGNITE IN HYDROGEN AND IN HELIUM DURING INITIAL REACTION STAGES

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INTRODUCTION

Light hydrocarbon yields obtained during the initial stages of coal gasification are of particular importance in affecting overall performances and thermal efficiencies of processes directed toward conversion of coal to pipeline gas. It is during this gasification stage that coals undergo devolatilization reactions leading to the formation of carbon oxides, water, oils and tars, and, most importantly, significant quantities of light hydrocarbons, particularly methane, in the presence of hydrogen at elevated pressures. Since, however, the exceptionally high reactivity most coals exhibit for methane formation during initial reaction stages is transient, existing only for a period of seconds at higher temperatures, rational design of commercial systems to optimize methane yields requires as detailed a kinetic characterization of pertinent processes occurring as is possible. Because of its importance, this reaction has been studied in a variety of experimental investigations, using fixed beds (1,5,6,7,10), fluidized beds (2,7,10), and dilute solid-phase systems (3,4,8,9,11,12). In spite of the extensive amount of information obtained from these studies, however, primary emphasis in the development of kinetic correlations has been placed on description of total methane yields obtained after relative deactivation of coal solids has occurred, rather than on the more detailed behavior occurring during the transient period of "rapid-rate" methane formation. Although this existing information is of significant value at one level of process design, it is primarily limited to application to large-scale systems in which reaction conditions closely parallel the laboratory conditions employed in obtaining the information.

This current investigation has, therefore, been stimulated by the need for additional information that quantitatively characterizes intermediate reaction processes occurring prior to completion of the "rapid-rate" methane formation reaction. In this study, a continuous dilute-phase transport reactor has been employed having the particularly unique feature of variable temperature control along the length of the reactor, which permits the establishment of various desired gas-solid, time-temperature histories.

This paper discusses some initial results obtained with this experimental system for gasification of Montana lignite in hydrogen, helium, and hydrogen-helium mixtures, under the more conventional conditions of isothermal operation, and under conditions of constant gas-solid heat-up rate ($\sim 50^{\circ}\text{F/s}$). Results are reported for tests conducted at temperatures from 900°F to 1550°F and pressures from 18 to 52 atmospheres.

EXPERIMENTALApparatus and Procedures

The composition of the Montana lignite used in this study is given in Table 1, and a schematic diagram of the experimental apparatus is shown in Figure 1. The main component of the experimental system is a helical-coiled

Table 1. FEED COMPOSITION
(Montana Lignite, Dry Basis)

	Mass, %
Ultimate Analysis	
Carbon	65.13
Hydrogen	4.13
Oxygen	24.20
Nitrogen	0.89
Sulfur	0.57
Ash	5.08
Total	100.00
Proximate Analysis	
Fixed Carbon	51.30
Volatile Matter	43.62
Ash	5.08
Total	100.00

transport reactor formed from a 1/16-inch-ID tube. General information describing the reactor coil is given in Table 2. The diameter of the coil is

Table 2. REACTOR-COIL DATA

Total Tube Length	200 ft
Tube ID	1/16 in.
Tube OD	1/8 in.
Tube Material	316 stainless steel, seamless
No. of Individually Controlled Heating Zones	9
Tube Length Per Zone	22.2 ft
Helix Dimensions	1-ft diameter X 2-1/2 ft high
Electrical Resistance per 22.2-ft Tube Section	1 ohm
Transformer Output	
Zones 1-6	35 volts, 35 A
Zones 7-9	40 volts, 40 A
Maximum Power Requirement for Transformers (total)	12 kW
Maximum Operating Temperature	1600°F
Maximum Design Pressure	1000 psi
Temperature Controller Type	Weathermeasure, TRA-1, Triac-Triggered SCR gate

about 1 foot, with a total tube length of 200 feet and a vertical reactor height of about 2-1/2 feet. With this design, gas flow rates of 5 to 50 SCF/hr and solids flow rates of 50 to 500 gph are possible. The relative gas-solids flow rates used in individual tests were such that solids/gas volume ratios were less than 0.02. The solids particles used in this system were relatively uniform in size, ranging in diameter from 0.0029 to 0.0035 inch. Such small particles flowed essentially at gas velocities, and calculated temperature differences between the gas and solids and between the reactor tube wall and the flowing gas-solids stream were negligible.

The reactor tube itself serves as the heating element, and electrodes are attached directly at various points along the length of the helical coil. Nine independent heating zones are thereby incorporated into the system to provide flexibility in establishing desired temperature profiles.

In a typical experimental test, the following operational procedures were generally used:

Initially, the system is brought to a desired pressure, and a preliminary temperature profile is established in the reactor coil by adjusting the controls for the nine heating zones. When feed-gas flow is established at a desired rate, the flow from the solids feed hopper is initiated. Solids are screwed into a mixing zone, there combining with the feed gas, and the resulting mixture then flows through the reactor coil. The temperature in the mixing zone is maintained equal to the temperature at the entrance of the coil — usually about 600°F. This is sufficiently high to inhibit steam condensation at the highest pressures used in this study, but low enough to inhibit any significant reaction of coal solid.

When both gas and solids flows are begun, the final desired temperature profile is established in the reactor tube. In the various tests conducted, the temperature either increased along the coil in the direction of gas-solids flow or was maintained at a constant value. For increasing temperatures, the temperature-versus-distance characteristic along the coil corresponded to a linear relationship between the temperature and the gas-solids residence time in the coil of about 50°F/s. In isothermal tests, gas-solids residence times ranging from 5 to 14 seconds were employed.

The hot gas-solids mixture exiting from the bottom of the reactor coil passes through an initial quench system that rapidly reduces its temperature to approximately 600°F to inhibit further reaction. At this point in the system, a lower temperature is avoided in order to prevent steam from condensing on the solids. The partially cooled mixture then proceeds through one of three solids filters, which retains the solids but permits gas flow. The gas continues through a condensor that removes water and oils and then passes through a gas-sampling panel, which is used intermittently to obtain gas samples for mass spectrographic analysis. In some of the tests conducted, the product gas was also continuously monitored with a Beckman Model 400 hydrocarbon analyzer to measure the total concentration of carbon in hydrocarbon species.

The data of primary interest in a given test corresponded to steady-state operation. Since a certain amount of time is required to achieve such operation, certain facilities are incorporated into the system to permit the collection of solid residues corresponding to steady-state operation but not contaminated with residues resulting from unsteady-state operation. To accomplish this, the product solids could be collected in any of the three solids filters, depending on the position of a multiple-exit hot valve (valve V2 in Figure 1). During unsteady-state operation, when the desired gas and solids flows and the temperature profile in the reactor coil were being established, the product gas and solids flows were directed through solids filter A. When steady-state conditions were established, the product gas and solids were directed through solids filter B, which then accumulated a solids residue for analysis. Before the end of some tests, a direct determination of the solids inventory in the reactor coil was made to estimate the average solids residence times. This was accomplished by simultaneously closing valve V1 at the top of the coil, stopping the screw feeder, and diverting the product gas and solids flow through solids filter C. Valve V1 is a hot valve fitted with a solids filter that stops solids flow but permits gas flow when in a closed position. After these simultaneous operations, the solids inventory in the reactor coil is accumulated in solids filter C. Average solids residence times computed from chemical analyses and weight measurements of these solids generally corresponded very closely to calculated gas residence times, indicating negligible gas-solids slippage in the reactor coil.

Data Analysis

The experimental system employed in this study is an integral system in the sense that the gas, liquid, and solids conversion determined by analyses of the reactor-coil exit streams are the result of chemical interactions occurring along the length of the coil under systematically varying environmental conditions. With this type of system, the information required for proper kinetic characterization includes definitions of the conversions and local environmental conditions along the entire length of the coil, not only at the exit. Although this information could not be obtained in a single experimental test, a good approximation was achieved by series of properly designed tests. The basis for design of such test series depended on the fact that the gas and solids were essentially in plug flow through the coil, and slippage of the solids relative to the gas flow was negligible, since, under these conditions, both gas and solids conversions could be expressed solely as a function of pressure, initial gas/solids feed ratio, temperature, and temperature-time history.

Individual tests in isothermal test series were conducted at the same temperature, pressure, feed gas/solid ratio, and feed gas composition, varying only total feed gas and solids flow rates to obtain results as a function of residence time. Individual tests in test series conducted at constant heat-up rate conditions were designed to obtain results as a function of final temperature at the same pressure, feed gas/solids ratio, feed gas composition, initial temperature, and heat-up rate. This was accomplished by varying the feed-gas flow rate and temperature profile in individual tests according to the following expressions:

$$G_o = \frac{\pi d^2 P L \alpha}{2R(T_f^2 - T_o^2)} \quad 1)$$

and

$$T = [T_o^2 + (T_f^2 - T_o^2) z/L]^{1/2} \quad 2)$$

where

- z = length at intermediate point along the reactor coil
- L = total length of reactor coil
- T_o = temperature at entrance of reactor coil
- T_f = temperature at reactor-coil exit (final temperature)
- T = temperature at intermediate point z along the reactor coil
- G_o = feed-gas flow rate (mol/time)
- R = gas constant
- d = reactor-tube diameter
- α = gas-solids heat-up rate
- P = pressure

With this approach, and in the absence of catalytic reactor wall effects, yields obtained in individual tests conducted at a constant heat-up rate at various final temperatures could be interpreted as approximating yields occurring along the length of the reactor coil in a single test conducted at the maximum final temperature employed.

The question of reactor-wall-catalyzed reactions was investigated in a series of preliminary tests with simulated feed gases in the absence of coal solids. The results of these tests indicated that the only reaction of significance that occurred in the presence of typical concentrations of the major gas species was the water-gas shift reaction, which was initiated at approximately 1200°F.

RESULTS

Feed-gas compositions used in individual test series are given in Table 3 along with a definition of notation to distinguish primary results obtained in these test series, as illustrated in Figures 2 to 12. This notation is also applicable to Figures 13, 14, 15, and 17. In the presentation of experimental results, various species and species groups that evolved during gasification have been categorized as follows:

- Carbon monoxide, carbon dioxide, hydrogen, methane, ethane, and benzene: Determined by mass-spectrographic analysis of dry product gases.
- Water: Computed as the difference between total oxygen gasified and oxygen present in carbon monoxide and carbon dioxide in the product gas.
- Unknown gaseous hydrocarbon: Computed as the difference between total carbon in gaseous hydrocarbon species, as determined by a hydrocarbon analyzer, and carbon present in methane, ethane, and benzene in the product gas.
- "Heavy hydrocarbon": Computed as the difference between total carbon gasified and carbon present in carbon monoxide, methane, and ethane.

The basis for this classification of species and species groups is related to the accuracies of analytical measurements in this study. Such measurements were limited by the fact that, in all tests conducted, the concentrations of reaction products in the dry product gas were less than 5% by volume (CO or CO₂, 0% to 1.5%; CH₄, 0% to 3%; C₂H₆, 0% to 0.8%; C₆H₆, 0% to 0.3%). These conditions were employed so that, in individual tests, the partial pressures of feed gas components were essentially constant throughout the length of the reactor coil, which facilitates quantitative kinetic analyses.

Table 3. FEED-GAS COMPOSITIONS

Notation in Figs. 2-15, 17	Feed Gas Pressure, atm			Temperature Profile	
	H ₂	He	Total	Isothermal	Constant Heat-up Rate
●	0	35	35		X
△	18	0	18		X
▲	18	17	35		X
□	35	0	35		X
▽	52	0	52		X
●	0	35	35	X	
△	18	0	18	X	
▲	18	17	35	X	
□	35	0	35	X	

The direct measurement of water yield in condensed liquid products was not usually accurate because of the relatively small amounts obtained and the uncertainty of the quantity of this species that was not condensed in the knockout pot. Computed values for the yield of this species are likely to be somewhat greater than actual yields because of the likelihood that some oxygen could be combined in oils and tars. This error, however, is probably small.

The measurement of concentrations of gaseous hydrocarbon species, other than methane and ethane, and to a lesser degree benzene, by mass-spectrographic analysis was difficult for the test conditions used because of the small molecular concentrations of individual species. Although measurements of benzene concentrations in the gas were sufficiently accurate to be meaningful,

the interpretation of this concentration in terms of total benzene yields is questionable because some of the benzene formed in the reactor coil may have condensed in the knockout pot, but later may have vaporized when the liquid products warmed to ambient temperatures prior to containment.

The unknown-gaseous-hydrocarbon group probably consists primarily of lighter aliphatic species such as ethylene, propane, propylene, butane, and butylene. The heavy-hydrocarbon group consists of the potentially condensable tars and oils, including benzene, and the unknown-gaseous-hydrocarbon species. In a few of the tests conducted, sufficient condensed hydrocarbon liquids were recovered to make direct experimental evaluations of total carbon balances. The fact that these balances showed better than 98% recovery suggests that, in the majority of tests in which insufficient liquids were recovered for quantitative analysis, the computed difference between the carbon in the heavy-hydrocarbon group and the carbon in the unknown-gaseous-hydrocarbon group probably is quite representative of the carbon in the actual condensed hydrocarbons, when benzene yields are negligible.

The results given in Figures 1 to 12 exhibit the following major trends:

Evolution of Major Coal Components: Carbon, Oxygen, and Hydrogen
(Figures 2, 3, and 4)

The evolution of total carbon from the coal solids generally increases with increasing temperature and hydrogen partial pressure, with conversions obtained for isothermal operation being greater than for operation at constant heat-up rate. Total oxygen evolution from coal solids also increases with increasing temperature, and although conversions obtained in hydrogen are greater than in helium, no significant effect of hydrogen partial pressure on conversion is apparent in the range from 18 to 52 atmospheres. As with total carbon conversion, total oxygen evolution is also greater under isothermal operation. Total evolution of hydrogen from the coal solids increases with increasing temperature and is greater in isothermal tests, but is not a significant function of hydrogen partial pressure. This is a particularly important result, indicating that hydrogen evolution is primarily a thermally activated phenomenon dependent only on time-temperature history.

It is also of significance that the results shown in Figures 2, 3, and 4 for operation with a hydrogen-helium mixture (hydrogen partial pressure = 18 atmospheres) are essentially identical to results obtained with pure hydrogen at a total pressure of 18 atmospheres. This similarity is also apparent in yields of gasified products and suggests that hydrogen partial pressure and not total pressure is the main parameter affecting kinetic behavior during the initial gasification stages of Montana lignite. A somewhat different effect has been observed in an investigation with bituminous coal by Anthony (1), where it was found that initial gasification yields tended to increase with increasing hydrogen partial pressure, but to decrease with increasing total pressure. This effect was explained as being due to increased diffusion resistance within the coal structure. This was not observed in this previous study with lignite, which does not become plastic during devolatilization.

Oxygen-Containing Product Species (Figures 5 and 6)

For tests conducted at a constant heat-up rate, total carbon dioxide evolution is completed below 1000°F (Figure 5). The amount evolved (about 0.029 g-mol/g-atom feed carbon) is essentially the same in hydrogen and in helium and is independent of hydrogen partial pressure. This amount is probably reflective of the concentration of carboxyl functional groups in the raw lignite. As temperature increases above 1000°F, the carbon dioxide yield remains substantially constant up to about 1200°F, then decreases with further increases in temperature for tests conducted in hydrogen, but increases with further increases in temperature for tests conducted in helium. These variations above 1200°F are probably due to the water-gas shift reaction, as suggested by results of tests conducted in the absence of coal solids. The dashed line shown in Figure 5B represents the assumed carbon dioxide yield for the case in which no water-gas shift occurs and was used as a basis for adjusting the total oxygen distribution in directly evolved species, as illustrated in Figure 6.

Hydrocarbon Product Species (Figures 7 to 12)

Methane-plus-ethane yields are highly dependent on hydrogen partial pressure (Figure 7). For tests conducted at a constant heat-up rate in hydrogen, methane-plus-ethane formation is slight below 1000°F (about 0.01 g-atom carbon/g-atom feed carbon). With further increases in temperature, yields in helium increase slightly, leveling off at a value of about 0.03 g-atom carbon/g-atom feed carbon above about 1300°F; in hydrogen, dramatic increases in methane-plus-ethane yields occur with increasing temperature. From about 1000° to 1200°F, this increase is about the same for hydrogen partial pressures from 18 to 52 atmospheres; above 1200°F, methane-plus-ethane yields increase with increasing hydrogen partial pressure, and yields at all pressures tend to suggest leveling off at higher temperatures. Reasonable extrapolation of the curves shown would indicate little increases in yields above about 1700°F for the reaction times employed.

Methane-plus-ethane yields obtained in isothermal tests are essentially independent of gas-solids residence times ranging from 5 to 14 seconds and are the same as yields obtained in constant heat-up rate tests at 1000° and 1400°F. This is true for tests conducted in hydrogen and in helium. At 1200°F, yields obtained in isothermal tests are somewhat greater than those obtained in constant heat-up rate tests.

The sum of methane plus ethane has been referred to in the above discussion instead of the yields of each species individually because of an apparent stoichiometric relationship between the formation rates of each species. One such indication is illustrated in Figure 8, which shows that ethane yields are approximately directly proportional to methane yields up to values of methane yields of about 0.06 g-atom carbon/g-atom feed carbon. At higher methane yields, ethane yields tend to approach a maximum and then decrease with further increases in methane yields, with the maximum increasing with increasing hydrogen pressure. This behavior can be explained by assuming that, at all temperature levels, ethane is formed in direct proportion to methane, but that, at sufficiently high temperatures (above about 1300° to 1400°F), ethane converts to methane in the presence of hydrogen.

The increasing maximum ethane yields with increasing hydrogen pressure can be explained by noting that these maxima occur at about the same temperature. This is demonstrated in Figure 9, which shows that the ratio of ethane-to-methane yield is apparently a function only of temperature and not pressure. This evidence suggests that hydrogen attack on lignite does not result in formation only of methane at any level of temperature, but rather results in a formation of both ethane and methane in a fixed ratio. Examination of data available in the literature (5, 6) suggests that this ratio tends to decrease with increasing coal rank.

The heavy-hydrocarbon yields shown in Figure 10 are substantially constant above 1000°F for tests conducted at constant heat-up rates, and yields obtained in hydrogen and in helium are generally similar. This species group, consisting of oils, tars, and light aliphatic gaseous species, apparently is formed below 1000°F, and although variations in the distribution of individual species within this group are likely at higher temperatures, there is apparently only limited transformation of species in this group to methane, ethane, or char, at least up to 1560°F. Heavy-hydrocarbon yields obtained in isothermal tests are significantly greater than those obtained in constant heat-up rate tests, particularly at 1400°F. This may primarily occur because, for isothermal operation, feed-coal solids heat up very rapidly to reactor temperature in the first few feet of the reactor coil. Assuming that most heavy-hydrocarbon formation occurs below 1000°F, increased heat-up rates through this range of temperature would tend to favor evolution of tars and oils, in competition with repolymerization in the solid phase. With this explanation, it is pertinent that increased isothermal temperature levels correspond to increased heat-up rates through the oil-tar formation range, being of the order of several thousand degrees per second at an isothermal temperature of 1400°F.

Figure 11 indicates that, in hydrogen, the unknown-gaseous-hydrocarbon yield decreases above about 1200°F. Although this decrease is not reasonably detectable in a corresponding decrease in the heavy-hydrocarbon yield, possibly because of data scatter, above 1200°F, light aliphatic species can reasonably be expected to begin to convert to ethane and methane in the presence of hydrogen. In helium, this conversion does not occur.

Semiquantitative indications of benzene yields (Figure 12) suggest that the heavier components in the oil-tar fraction begin to convert to benzene at about 1300°F, with substantial conversions being achieved by 1450°F. No benzene was detected in gas analyses for any test conducted below 1270°F with hydrogen, nor at any temperature for tests conducted in helium, suggesting that benzene is not a significant fraction of the oils and tars that initially evolve below 1000°F.

Relationship Between Equivalent Methane-Plus-Ethane Yield and Hydrogen Gasified

Figure 13 shows that, at any hydrogen pressure, "equivalent" methane-plus-ethane yields are directly proportional to the amount of hydrogen gasified. Equivalent methane-plus-ethane yields represent the difference between actual methane and ethane yields and an adjustment term obtained

from Figure 11 at a corresponding temperature. The correction term is the difference between values of the unknown-gaseous-hydrocarbon yield indicated by the dashed line and the solid line. The basis for this correction is the assumption that the unknown-gaseous-hydrocarbon group consists of relatively low-molecular-weight aliphatic species (other than methane and ethane), which hydrogenate to form ethane and methane at increased temperatures in the presence of gaseous hydrogen. Because a relationship is sought to characterize methane and ethane formation only as derived directly from the coal or coal char, the estimated amount of methane and ethane formed from gaseous interactions was subtracted from total methane-plus-ethane yields.

The relationship shown in Figure 13 is a very important one. It indicates that, at any hydrogen partial pressure, methane and ethane evolve directly in proportion to the total amount of hydrogen evolved from the coal, although the proportionality increases significantly with increasing pressure. It should be recalled that results given in Figure 4 show that total hydrogen evolution is not a function of hydrogen partial pressure and is essentially identical in hydrogen and in helium. This combined evidence suggests then that the formation of active sites that catalyze methane and ethane formation in the presence of hydrogen is directly related to the process in which coal hydrogen is released, this latter process being independent of gaseous atmosphere and dependent only on time-temperature history. A model for quantitatively correlating equivalent methane and ethane formation rates from coal solids, based on the evidence discussed, is presented in the final section of this paper.

CORRELATION OF "RAPID-RATE" METHANE AND ETHANE FORMATION

In consideration of the data obtained in this study with Montana lignite, the following model is proposed to describe the kinetics of methane and ethane formation during initial stages of gasification.

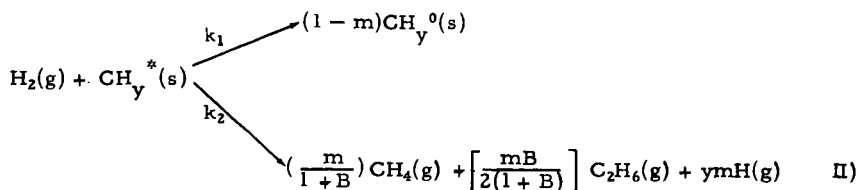
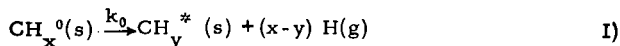
During heat-up of raw lignite (Structure A), interactions within the coal initially occur below 1000°F and result primarily in the evolution of a) carbon dioxide, probably resulting from gasification of all carboxyl functional groups; b) some water and carbon monoxide; c) some relatively low molecular weight aliphatics; and d) oils and tars. These reactions are essentially pyrolysis reactions that occur because of the breaking of certain of the weaker side-chain bonds as well as bonds connecting relatively large polyatomic molecules in the carbon matrix. This latter process results in the intermediate formation of large fragments, possibly free radicals, which then either a) become stabilized because of hydrogen disproportionation or interaction with gaseous molecular hydrogen and evolve as oils and tars, or b) polymerize to form an intermediate type of solid (Structure B). The total amounts of materials other than oils and tars that gasify below 1000°F are essentially independent of gas atmosphere or heat-up rate, suggesting a stoichiometric relationship between the individual species formed and the functional groups present in the raw lignite. Total oil and tar formation is similar in hydrogen and in helium, and increases with increasing heat-up rate, which is apparently a result of the competition between stabilization and polymerization of intermediate free-radical fragments.

Between 1000° and 1300°F, most of the remaining oxygen in the coal is evolved as carbon monoxide and water, with water formation being slightly greater in hydrogen than in helium. The gasification of hydrogen from the coal solids is relatively small between 1000° and 1200°F, being due to the formation of water and some methane and ethane in the presence of gaseous hydrogen and both water and hydrogen in the presence of helium. Above 1200°F, evolution of coal hydrogen begins to increase rapidly with increasing temperature, accompanied by a rapid increase in the formation of methane and ethane in the presence of gaseous hydrogen.

The removal of oxygen between 1000° and 1300°F can be considered to correspond to the transition of the main carbon matrix from Structure B to a second intermediate main structure (Structure C). Structure C is considered to be comprised primarily of carbon and hydrogen and, with increases in temperature above about 1200°F, converts to a relatively stable "char" structure (Structure E) through the evolution of hydrogen. During this transition, however, Structure C initially converts to an active intermediate structure. Structure D, as hydrogen is evolved, and Structure D then can either convert to the stable char structure, Structure E, or interact with molecular hydrogen to form methane and ethane.

The following quantitative representation of the steps leading to methane and ethane formation assumes for simplicity that all oxygen is gasified prior to the formation of methane and ethane as a result of interactions of gaseous hydrogen with Structure B. Although the experimental data indicate some overlap between the final stages of oxygen gasification and the initial stages of methane and ethane formation between 1200° and 1300°F, this assumption does not appreciably alter the quantitative evaluation of the parameters derived based on the model proposed.

The processes that lead to "rapid-rate" methane and ethane formation are assumed to occur according to the following overall reactions:



where

- CH_x^0 = solid component resulting from interactions occurring during primary pyrolysis (Structure C)
- CH_y^* = intermediate solid active species (Structure D)
- H = hydrogen evolved from solids in Reactions I and II
- CH_y^0 = product coal char (Structure E)

- H_2 = gaseous molecular hydrogen
 x = atomic ratio of hydrogen to carbon in CH_x^0
 y = atomic ratio of hydrogen to carbon in CH_y^0 and CH_y^*
 B = carbon ratio of ethane to methane formed in Reaction II
 m = fraction of carbon in CH_y^* converted to methane and ethane in Reaction II
 k_0, k_1, k_2 = first-order rate constants
 s = solid
 g = gas.

Let -

- λ = fraction of feed carbon as CH_x^0 when conversion to Structure C is complete, g-atom carbon/g-atom feed carbon
 n_C^* = equivalent methane and ethane formed from coal at any time during gasification, g-atom carbon/g-atom feed carbon
 n_C^0 = equivalent methane and ethane formed by pyrolysis reactions prior to the onset of Reaction I, g-atom carbon/g-atom feed carbon
 f = fraction of CH_x^0 converted via Reaction I at any time during gasification
 n_H^* = total coal hydrogen gasified at any time, g-atom hydrogen/g-atom feed carbon
 n_H^0 = hydrogen gasified via pyrolysis reactions prior to the onset of Reaction I, g-atom hydrogen/g-atom feed carbon

Based on the definitions given above, it is possible to determine certain of the unknown stoichiometric parameters which characterize the model assumed, prior to consideration of the kinetics of Reaction I. In these evaluations, it is assumed that the ratio k_2/k_1 is independent of temperature.

According to the above definitions -

$$f = (n_C^* - n_C^0)/m\lambda \quad 3)$$

and

$$f = (n_H^* - n_H^0)/(x - y + ym)\lambda \quad 4)$$

Combining Equations 3 and 4 and rearranging leads to -

$$n_C^* = mn_H^*/(x - y + ym) + \{n_C^0 - n_H^0[m/(x - y + ym)]\} \quad 5)$$

Letting $S = m/(x - y + ym)$ and $I = [n_C^0 - n_H^0m/(x - y + ym)]$, Equation 5 can be represented as -

$$n_C^* = Sn_H^* + I \quad 6)$$

Thus, where m is constant, a plot of n_C^* versus n_H^* , both experimental parameters, should yield a straight line with a slope equal to S and intercept at $n_H^* = 0$ of 1. Figure 13 shows such a plot for data obtained in constant heat-up rate tests in helium and in hydrogen. Values of S increase with increasing pressure because of increasing values of m with increasing pressure. The common point of intersection of the lines drawn corresponds to values of $n_C^0 = 0.01$ g-atom carbon/g-atom feed carbon, and $n_H^0 = 0.272$ g-atom hydrogen/g-atom feed carbon. Table 4 tabulates the values of S obtained from Figure 13 as a function of hydrogen partial pressure, P_{H_2} .

Table 4. VARIATION IN S WITH P_{H_2}

P_{H_2} , atm	S , g-atom carbon/ g-atom hydrogen
0	0.084
18	0.352
35	0.514
52	0.649

Now, let —

Y_C = total carbon in partially gasified lignite, g-atom carbon/
g-atom feed carbon

Y_H = total hydrogen in partially gasified lignite, g-atom hydrogen/
g-atom feed carbon

$Z = Y_H/Y_C$ = hydrogen/carbon ratio in partially gasified lignite,
g-atom hydrogen/g-atom carbon.

From the stoichiometry defined in Reactions I and II, Z is given by the expression —

$$Z = \frac{x - f(x - y + ym)}{1 - fm} \quad 7)$$

Solving for f in Equation 7 results in —

$$f = (x - Z)/(x - y + ym - mZ) \quad 8)$$

Equating the expression for f in Equation 8 to the expression for f in Equation 3 leads to —

$$(n_C^* - n_C^0)/\lambda m = [(x - Z)/m] / [(x - y + ym)/m - Z] \quad 9)$$

Rearranging Equation 9 and substituting S for the expression defined results in -

$$(n_C^* - n_C^0) (1/S - Z) = \lambda (x - Z) \quad (10)$$

Thus, a plot of the term on the left-hand side of Equation 10 versus Z should result in a straight line with a slope equal to $-\lambda$ and an intercept at $Z = 0$ of λx . Figure 14 shows such a plot for constant heat-up rate tests conducted in hydrogen. Data obtained with helium were not included in this plot because of the scatter that results from small values of S, which magnify variations in the term $(n_C^* - n_C^0)$. In accordance with the model assumed, data obtained at hydrogen partial pressures of 18, 35, and 52 atmospheres are reasonably correlated with a single straight line corresponding to a value of $\lambda = 0.83$ g-atom carbon/g-atom feed carbon, and a value of $x = 0.578$ g-atom hydrogen/g-atom carbon. The value of λ was not determined by a least-squares fit of the data, but was "forced" so that the amount of carbon initially present in the component CH_x^0 is equal to the total amount of carbon initially present in the raw lignite, less the total carbon evolved during pyrolysis due to formation of carbon monoxide, carbon dioxide, and the heavy-hydrocarbon species. Note that if the component CH_x^0 consisted of polycondensed aromatic units of hexagonally arranged carbon, with hydrogen present on lattice edges, then the value of $x = 0.578$ corresponds to an average ring number of 5.

The value of y is assumed to be 0.25 g-atom hydrogen/g-atom carbon, based on measurements made of hydrogen contents of Montana lignite chars gasified at elevated temperatures for extended times. With this assumption, values of m can be computed for corresponding values of S obtained from Figure 13, according to the expression -

$$m = S(x - y)/(1 - Sy) \quad (11)$$

In addition, values of $r = k_2/k_1 = m/(1 - m)$ can also be computed. Values of m and r are given in Table 5 as a function of hydrogen pressure for constant heat-up rate tests.

Table 5. VARIATION OF m AND r WITH P_{H_2}

P_{H_2} , atm	m	r
0	0.028	0.029
18	0.127	0.145
35	0.194	0.240
52	0.254	0.341

The values of r given above increase with increasing hydrogen partial pressure. Figure 15 shows, in fact, a linear relationship between r and P_{H_2} , which is represented by the expression -

$$r = 0.03 + 0.00605 P_{H_2} \quad (12)$$

Thus, all the parameters necessary to quantitatively characterize the model assumed have been determined, except for parameters indicative of the kinetics of Reaction I. After complete conversion of the reaction intermediate, CH_x^* , however, the maximum methane-plus-ethane yield is independent of the kinetics of Reaction I and can be expressed as a function of the hydrogen partial pressure by the following expression:

$$\text{Maximum methane-plus-ethane yield, g-atom carbon/g-atom feed carbon} = \frac{0.83(0.029 + 0.00587P_{H_2})}{1 + 0.00587P_{H_2}}$$

It is of interest that the empirical form of the above expression is essentially the same as an expression proposed by Zahradnik *et al.* (12) to relate total methane yield as a function of hydrogen partial pressure during the initial hydrogenation of coals.

The following assumptions were made, consistent with results obtained in both constant heat-up rate and isothermal tests, to describe the kinetics of Reaction I:

1. CH_x^0 reacts according to Reaction I by a first-order process, but where there is a distribution of activation energies for the first-order rate constant, k_0 .
2. The distribution function of activation energies is a constant; i. e., $f(E)dE$ = fraction of total carbon in which the activation energy E in the rate constant,

$$k_0 = k_0^0 \exp(-E/RT)$$

is between E and $E + dE$

where -

$$\begin{aligned} f(E) &= 0 \text{ for } E < E_0 \\ f(E) &= C \text{ (constant) for } E_0 \leq E \leq E_1 \\ f(E) &= 0 \text{ for } E > E_1 \\ k_0^0 &= \text{preexponential factor} \end{aligned}$$

Note that because -

$$\int_{E_0}^{E_1} C \, dE = 1$$

then -

$$C = 1/(E_1 - E_0)$$

From these assumptions, the average conversion fraction of CH_4^0 can be expressed by the following relationship for any time-temperature history:

$$1 - f = \frac{1}{E_1 - E_0} \int_{E_0}^{E_1} \left\{ \exp \left[-k_0^0 \int_0^{\theta} \exp(-E/RT) d\theta \right] \right\} dE \quad 14)$$

where -

- θ = time
- T = absolute temperature
- R = gas constant.

For the specific case of constant heat-up rate, where $\alpha = dT/d\theta$, then Equation 14 can be expressed as the following:

$$1 - f = \frac{1}{E_1 - E_0} \int_{E_0}^{E_1} \left\{ \exp \left[-\frac{k_0^0}{\alpha} \int_{T_0}^T \exp(-E/RT) dT \right] \right\} dE \quad 15)$$

For isothermal conditions, Equation 14 has the form -

$$1 - f = \frac{1}{E_1 - E_0} \int_{E_0}^{E_1} \left\{ \exp \left[-k_0^0 \theta \exp(-E/RT) \right] \right\} dE \quad 16)$$

The best fit of our experimental data was obtained with the following values of E_0 , E_1 , and k_0^0 :

$$\begin{aligned} E_0 &= 79,500 \text{ cal/g-mol} \\ E_1 &= 118,100 \text{ cal/g-mol} \\ k_0^0 &= 7 \times 10^{20} \text{ s}^{-1} \end{aligned}$$

Experimental and calculated equivalent methane-plus-ethane yields are compared in Figure 16, where calculated yields were determined based on the parameters given above, using the appropriate correlation form for isothermal or constant-heat-up rate operation.

In summary, the correlations described in this paper provide a basis for predicting methane and ethane yields as a function of temperature, hydrogen partial pressure, and time-temperature history during the gasification of Montana lignite. Although these correlations were developed based on data obtained in hydrogen, helium, and hydrogen-helium mixtures, the results of a previous thermogravimetric study conducted at the Institute of Gas Technology (7, 10) showed that "rapid-rate" methane formation kinetics with air-pretreated bituminous coal are a function of hydrogen partial pressure even in gas mixtures containing other synthesis gas species, which may also be the case for the Montana lignite used in this current study. The generality of the parameters evaluated is, of course, not known because experimental results obtained only with Montana lignite were used in the development of the model. Although future studies are anticipated using other coals to evaluate this aspect, there is some evidence currently available from studies conducted at the U. S. Bureau of Mines, reported by Feldmann et al. (4), in which results obtained for hydrogasification of raw bituminous coals in a 3-inch-ID transport reactor show a strong similarity to corresponding results obtained in this study with Montana lignite. Figure 17, for example, compares methane and ethane yields obtained under isothermal temperature operation as a function of temperature for the two studies considered,* at approximately corresponding average hydrogen partial pressures.

The results shown indicate that relatively minor adjustments in one or two of the parameters defined in the model proposed in this paper would be required to fit the data obtained with the bituminous coals and the North Dakota lignite.

Another data comparison is shown in Figure 18, which plots total methane and ethane yields versus total coal hydrogen evolution for these same coals. Although the model proposed predicts linearity in these relationships only when referring to "equivalent" methane-plus-ethane yields and only when total oil/tar yields do not vary, the results shown are nevertheless suggestive that equivalent methane-plus-ethane yields obtained with the bituminous coals are essentially proportional to coal hydrogen evolution, as was indicated in this study with Montana lignite.

ACKNOWLEDGMENT

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*

The study at the U. S. Bureau of Mines was conducted under integral conditions, and the results presented correspond to operation with hydrogen-methane feed-gas mixtures. The average hydrogen partial pressure indicated in Figure 17 is the linear average of the feed and product gases.

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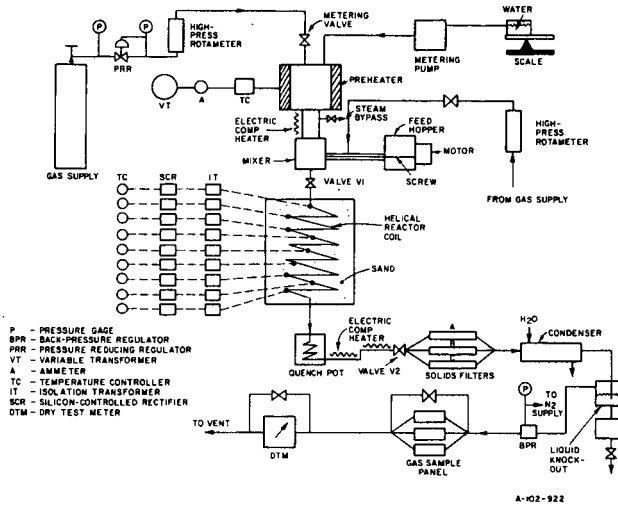


Figure 1. DIAGRAM OF THE EXPERIMENTAL SYSTEM

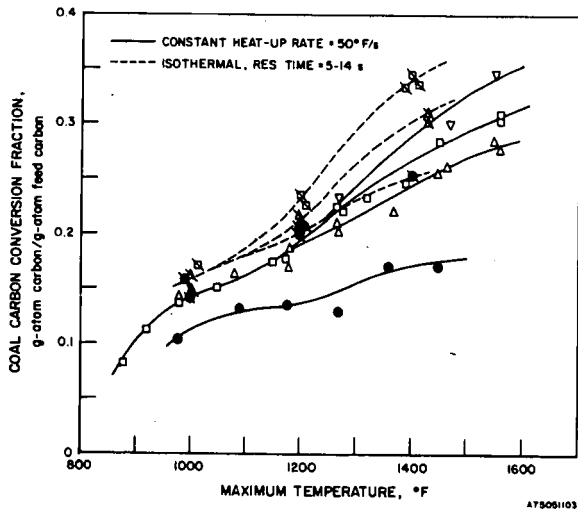


Figure 2. COAL CARBON CONVERSION

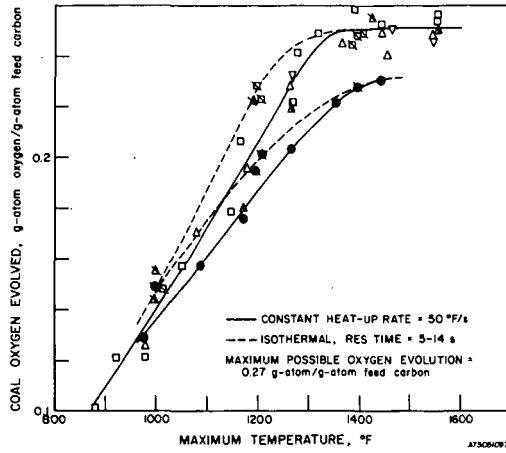


Figure 3. COAL OXYGEN CONVERSION

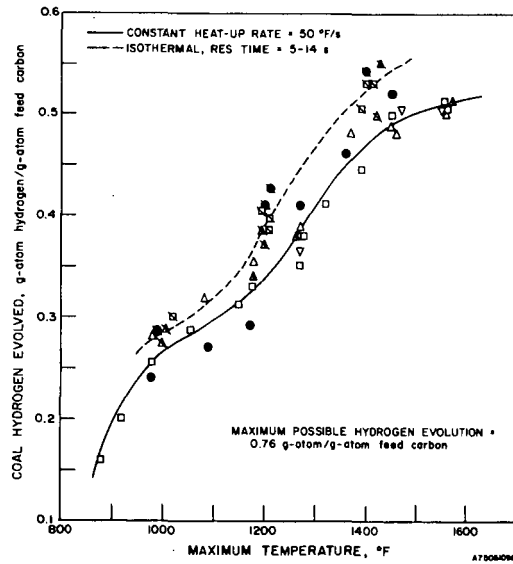


Figure 4. COAL HYDROGEN CONVERSION

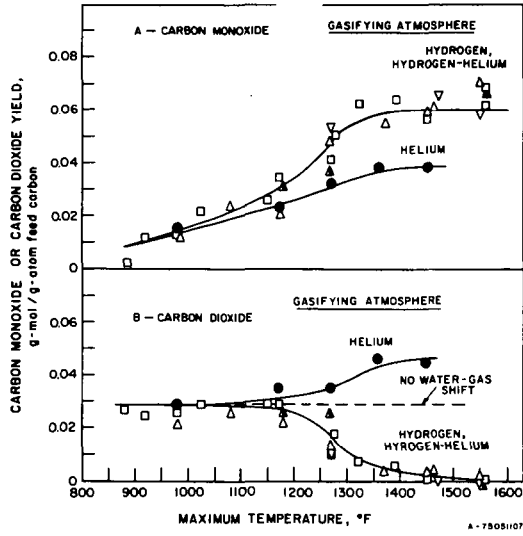


Figure 5. CARBON MONOXIDE AND CARBON DIOXIDE YIELDS

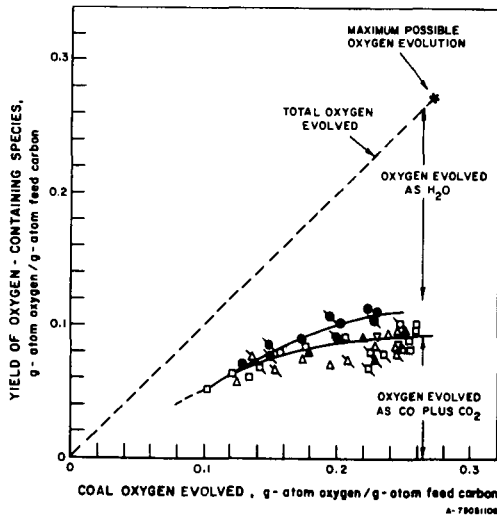


Figure 6. ADJUSTED EVOLVED OXYGEN DISTRIBUTION

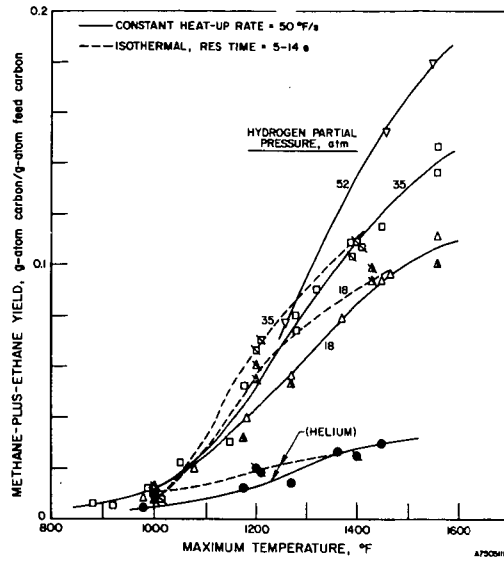


Figure 7. METHANE-PLUS-ETHANE YIELDS

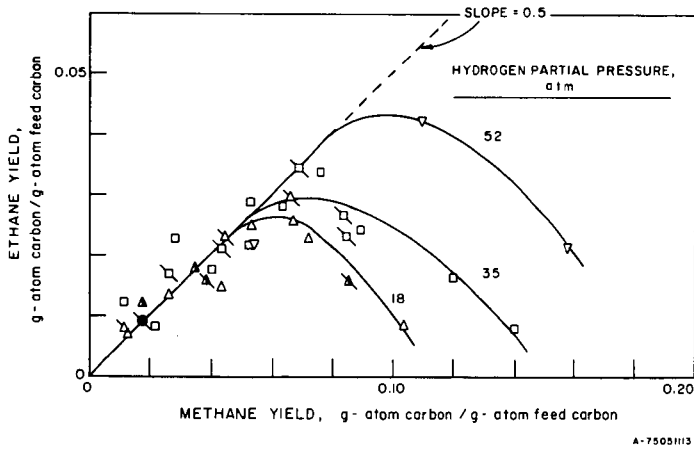


Figure 8. RELATIONSHIP BETWEEN METHANE AND ETHANE YIELDS

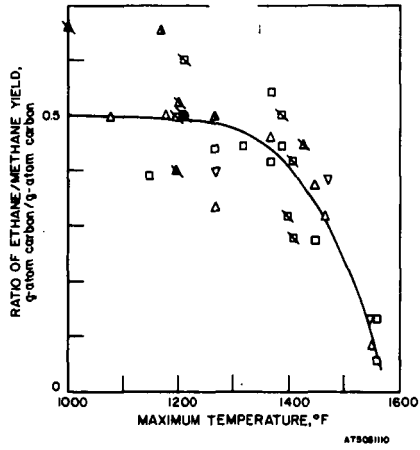


Figure 9. EFFECT OF TEMPERATURE ON ETHANE/METHANE RATIO

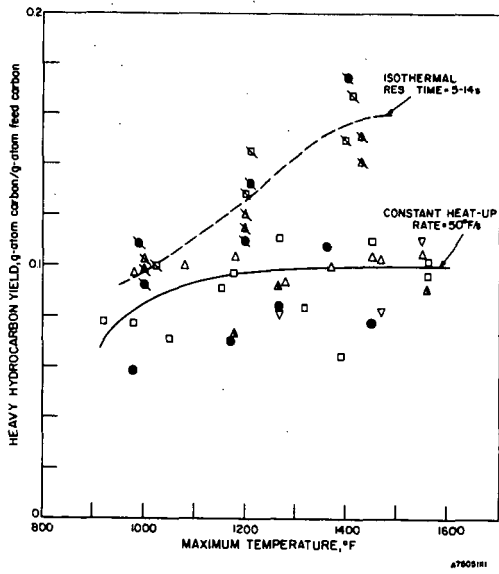


Figure 10. HEAVY-HYDROCARBON YIELDS

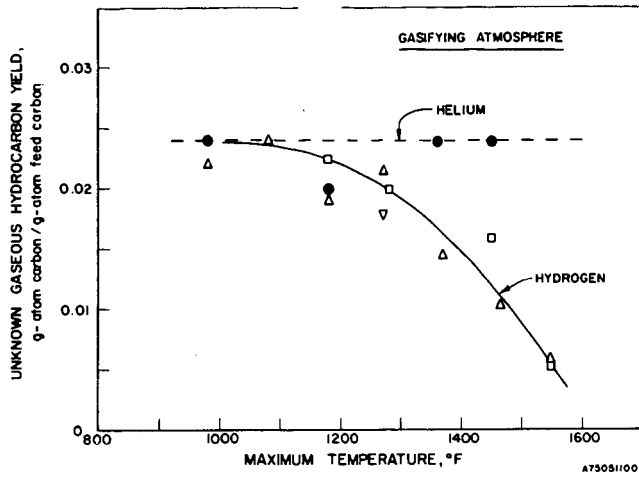


Figure 11. UNKNOWN-HYDROCARBON YIELDS

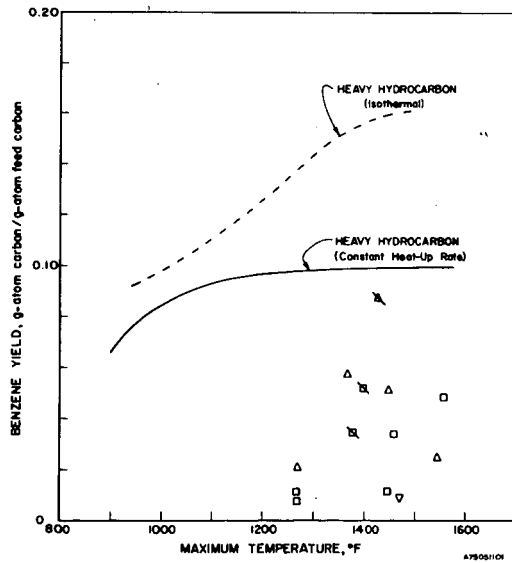


Figure 12. BENZENE YIELDS

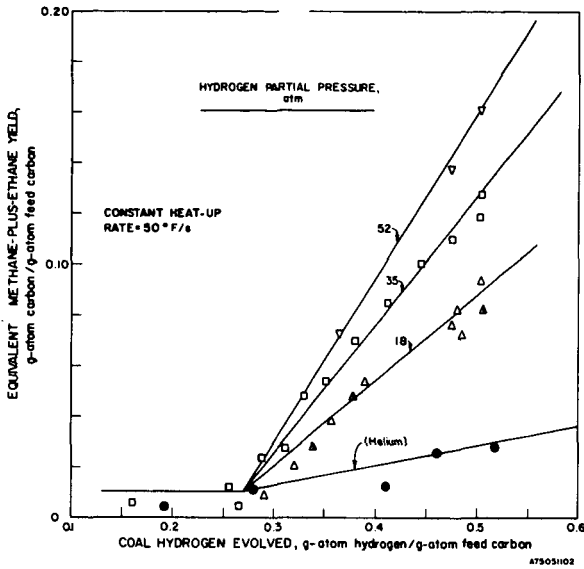


Figure 13. STOICHIOMETRIC RELATIONSHIP BETWEEN EQUIVALENT METHANE-PLUS-ETHANE YIELD AND COAL HYDROGEN CONVERSION

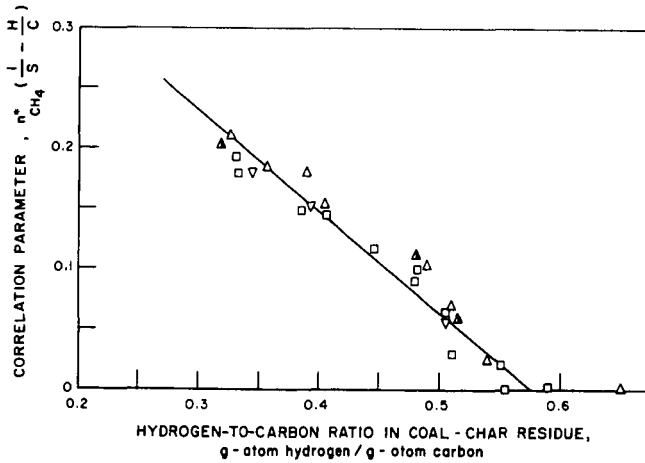


Figure 14. RELATIONSHIP BETWEEN STOICHIOMETRIC CORRELATION PARAMETER AND COAL HYDROGEN-TO-CARBON RATIO

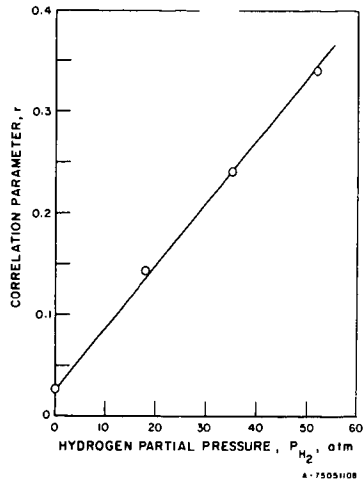


Figure 15. EFFECT OF HYDROGEN PARTIAL PRESSURE ON KINETIC PARAMETER, r

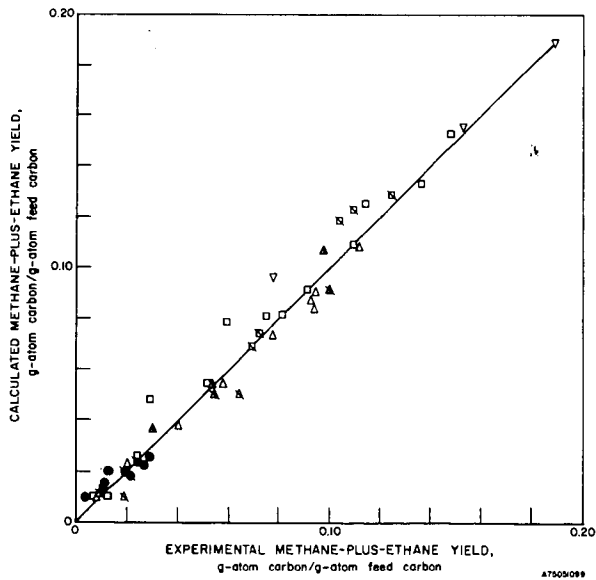


Figure 16. COMPARISON OF CALCULATED AND EXPERIMENTAL METHANE-PLUS-ETHANE YIELDS

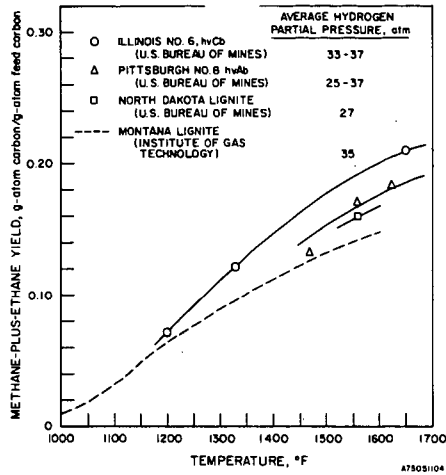


Figure 17. COMPARISON OF METHANE-PLUS-ETHANE YIELDS WITH DIFFERENT COALS

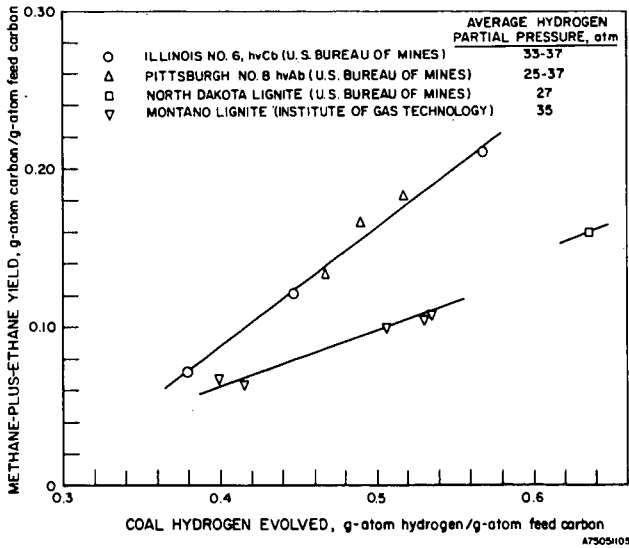


Figure 18. COMPARISON OF METHANE-PLUS-ETHANE YIELDS VERSUS COAL HYDROGEN CONVERSION CHARACTERISTICS FOR DIFFERENT COALS